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Research Article

Excess Molar Volume and Deviations in Viscosity of the Binary Liquid Mixtures Containing 1,3-Dioxolane + Alkanols at T = 298.15k

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Abstract

Thermodynamic and transport properties of liquid and liquid mixtures have been used to understand the intermolecular interactions between the components of the mixture. The sound velocity, density and viscosity of binary liquid mixtures are important from practical and theoretical point of view to understand the liquid theory. In the present study sound velocity, density and viscosity have been measured of binary mixtures of 1, 3-dioxolane with pentanol, hexanol, heptanol, octanol, nonanol and decanol over the entire range of mole fraction at 298.15K, and atmospheric pressure. From these experimental measurements the excess molar volume (V_m^E), excess viscosity (η^E), acoustic impedance (Z^E) and excess adiabatic compressibility (β_{ad}^E), have been calculated. The excess molar volume (V_m^E), excess viscosity (η^E), acoustic impedance (Z^E) and excess adiabatic compressibility (β_{ad}^E), have been analyzed in terms of interactions arising due to structural effect, charge-transfer complexes and dipole-dipole interaction between unlike molecules. These deviations have been correlated by a polynomial Redlich-Kister equation. The excess properties are found to be eighter negative or positive depending on the molecular interactions and nature of the liquid mixtures. Excess properties provide important information in understanding the solute-solvent interaction in a solution. The excess molar volume (V_m^E), excess viscosity (η^E), acoustic impedance (Z^E) and excess adiabatic compressibility (β_{ad}^E), values have been interpreted to terms of the nature of intermolecular interactions between constituent molecules of mixtures.

Keywords

1, 3-dioxolane, Mole Fraction, Excess Viscosity, Adiabatic Compressibility, Density, Sound Velocity, Molecular Interaction

1. Introduction

The sound velocity (u), density (ρ) and viscosity (η) of binary liquid mixtures are used experimentally to understand molecular interaction between the components of the mixtures and find applications in several industries and cosmetics [1-3]. The variation of sound velocity and other ultrasonic parameters of binary liquid mixtures have been studied by many researchers and thy have shed height upon structural changes associated with liquid mixtures of weakly and strongly components [4-10]. Ultrasound is a useful tool in nearly every case where a liquid and a solid must react. Furthermore, since ultrasound can radiate through large volumes of liquid, it is well suited for industrial applications. For these reasons future applications of ultrasound in chemical reactions will be in diverse. In the synthesis of pharmaceuticals,

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ultrasound will improve chemical yields over conventional methods [11, 12].

Objects of the present research find wide application in large scale operation of chemical production process. Ethers have wide use as commercial solvents and extractant foe esters, gum, hydrocarbons, alkaloids, oils, plastics, lacquers and paints. They are used as dewaxing extractants for lubricating oils. The physical properties of binary mixtures are studied for many reasons, the most important of which is to provide information about molecular interactions present in the liquid state. Experimental data of physical properties such of densities, viscosities, or refractive indices are required for a full understanding of the thermodynamic properties of liquid mixtures, as well as for practical chemical engineering work. The studied of excess thermodynamic properties are of considerable interest in understanding the intermolecular interactions in binary liquid mixtures. Knowledge of these properties is very important in many practical problems concerning mass transport and fluid flow. Physical properties of binary organic mixtures have been extensively studied in the literature of solution chemistry in view of the importance of such data in many areas of science and engineering. The ultrasonic investigations of pure liquids and liquid mixtures consisting polar & non-polar components are considerable importance in analyzing intermolecular interaction between component molecules. These studies find several applications in industries. Such studies as variations in concentration and temperature are use fulin giving insight in to structure and various bonding of associated molecular complexes and other related molecular processes. Ultrasonic velocity and related thermodynamic parameters helps us for characterizing thermodynamic and physico-chemical aspects of binary liquid mixtures such as molecular association and dissociation. Thermodynamic studies of binary liquid mixtures have attracted much attention of scientists. These physico-chemical analyses are used to handle the mixtures of hydrocarbons, alcohols, aldehydes, ketones etc. The measurement of ultrasonic speed enables us to the accurate measurement of some useful acoustic and thermodynamic parameters and their excess values. These excess values of ultrasonic velocity, adiabatic compressibility, molar volume and viscosity in binary liquid mixture are useful in understanding the solute-solvent interactions.

The present paper is a part of our ongoing research program in the measurement of thermodynamic and transport properties of binary liquid mixtures. The liquids were chosen in the present investigation on the basis of their industrial impotence.1,3-dioxolane (cyclic diether) have played a major role in the pharmaceutical chemistry. Therefore, the applications of these compounds attract us to study their behavior in alcohols. Alcohols are used as hydraulic fluids in pharmaceutical and cosmetics, in medications for animals, in manufacturing of perfumes, paint removers, flavors and dyestuffs, as defrosting and as an antiseptic agent. The experimental results have been used to discuss the nature of interaction between unlike molecules in terms of hydrogen bonding, dipole-dipole interactions and dispersive forces. It is well known that ethers interact with alcohols by dipole-dipole interaction, formation of new hydrogen bonds or hetro-associations and dispersion forces.

In the present paper several parameters such as adiabatic compressibility (β_{ad}), molar volume (V_m) and acoustic impedance (Z) of a binary system 1,3-dioxolane with pentanol, hexanol, heptanol, octanol, nonanol and decanol have been reported using the experimental values of sound velocity (u), density (ρ) and viscosity (η) of the binary liquid mixtures at temperature 298.15K. These results have been fitted to the Redlich-Kister polynomial equation.

2. Experimental Procedure

2.1. Chemicals

The source and purity of the chemical compound are shown in table 1. The substances density, viscosity and ultrasonic velocity is compared with the literature data (Table 2) to ascertain the purity, and a good agreement between the experimental data and literature data [13-24] was observed.

2.2. Apparatus and Procedure

All six binary liquid mixtures were prepared by weighing appropriate amounts of pure liquids on a digital electronic balance (Citizen Scale (I) PVT. LTD. Mumbai, India.) with a precision ± 0.1. The experimental uncertainty in mole fractions did not exceed ±0.0005. All the solutions were prepared by mass ratios and stored in the air-tight stopper measuring flasks. Experimentally measured densities, sound velocity and viscosities of the pure compounds compared well with their respective literature values shown in table 2 [13-24].

Table 1. *CAS Registry Number, Mass Fraction Purity of the chemicals.*

Component	Formula	CAS Reg. No.	Supplier	Mass Fraction Purity (%)	Method Purity analysis method
1,3-Dioxolane	C_3H6O_2	646-06-0	CDH Delhi	99.7	Chromatography by the supplier
Pentanol	$C_5H_{12}O$	71-41-0	CDH Delhi	99.7	Chromatography by the supplier
Hexanol	$C_6H_{14}O$	111-27-3	CDH Delhi	99.5	Chromatography by the supplier

Component	Formula	CAS Reg. No.	Supplier	Mass Fraction Purity (%)	Method Purity analysis method
Heptanol	C_7H16O	111-70-6	CDH Delhi	99	Chromatography by the supplier
Octanol	$C_8H_{18}O$	111-87-5	CDH Delhi	99.7	Chromatography by the supplier
Nonanol	$C_9H_{20}O$	143-08-8	CDH Delhi	99	Chromatography by the supplier
Decanol	$C_{10}H_{22}O$	112-30-1	CDH Delhi	99	Chromatography by the supplier

Table 2. *Comparison of Experimental and Literature density (ρ), sound velocity (u) and viscosity (η) of pure Components with Available Literature Values at T = 298.15K and atmospheric pressure.*

Compound	ρ (g.cm^{-3})		u (m.s^{-1})		η (mPa s)	
	This work	Literature	This work	Literature	This work	Literature
1,3-Dioxolane	1.0616	1.0577[17] 1.0586[17]	1340	1338[17] 1338[18]	0.5885	0.5878[17] 0.5873[17]
Pentanol	0.8124	0.8108[13] 0.8107[13]	1198	1197[16] 1268[22]	3.3978	3.5411[13] 3.5424[13]
Hexanol	0.8176	0.8187[13] 0.8152[15]	1306	1304[15] 1303[15]	4.6091	4.5924[13] 4.5932[13]
Heptanol	0.8196	0.8187[13] 0.8197[19]	1325	1327[15] 1327.37[24]	5.9066	5.9443[13] 5.94432[24]
Octanol	0.8236	0.8216[13] 0.8218[13]	1350	1348[14] 1347[22]	7.1508	7.6605[13] 7.5981[13]
Nonanol	0.8248	0.8244[15] 0.824224[15]	1366	1365[15] 1364[24]	8.9258	9.0230[21] 9.0200[24]
Decanol	0.8292	0.8267[15] 0.8264[19]	1378	1380[15] 1379[24]	11.8027	11.825[15] 11.829[15]

2.3. Measurements

Density:

Densities of pure liquids and their binary mixtures were determined by using a 25-ml specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kg.m^{-3}, is used to measure the densities (ρ) of pure liquids and binary mixtures. The specific gravity bottle filled with air bubbles free liquids is kept in a thermostate water bath controlled (MSI Goyal Scientific, Meerut.) with a thermal stability of ±0.01 K for over 30 minute to attain thermal equilibrium. The precision of the density measurements was estimated to be ±0.0002 g cm^{-3}.

The mixtures were prepared by mixing known volumes of the pure liquids in air-tight stoppered bottles. The weights were taken on a digital electronic balance (Citizen Scale (I) PVT. LTD. Mumbai, India) with a precision ± 0.1.

Sound velocity:

Ultrasonic velocity of the sample were measured at 298.15 K and atmospheric pressure using F-80D multifrequency ultrasonic interferometer (M/s Mittal Enterprises, New Delhi) at a constant frequency of 3 MHz. The sample were kept in the cell of interferometer and closed by rotating clock wise upper part of the cell having micrometer with least constant ±1.0 ×10^{-5} m. The minimum amount of the liquid needed was about 1.2 ×10^{-2} litre. The micrometer was slowly moved upward and first reading was taken when the current meter shows a maximum. The micrometer is further moved upward till 20 such maxima were passed on and the two reading gives total distance, d to be used in eq. (u = d. 103 ms^{-1}) for the evaluation of sound velocity. The temperature of the experimental solutions was maintained about 298.15 K and atmospheric pressure by circulating water around the cell with the

help of a pump from a thermostate regulated at required temperature to better than ±0.03K. The average of the two measurement of ultrasound velocity for each sample was taken which were accurate to ±0.03%. The measured values of ultrasonic velocities of pure1,3-dioxolane with pentanol. Hexanol, heptanol, octanol, nonanol and decanol compare well with the corresponding literature values.

Viscosity:

The viscosity of pure liquids and their binary mixture were measured using a Ostawald's viscometer having a capacity of about 25 ml and the capillary having a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow time of pure liquids and liquid mixtures and is was calibrated with triply distilled water, methanol and benzene at 298.15 K. The efflux time was measured with an electronic stop watch (Racer) with a time resolution (±0.015), and an average of at least four flow time readings was taken. Glass stopper was placed at the opening of the viscometer to prevent the loss due to evaporation during measurements. The two bulbs reservoir, one at the top and other at the bottom of the viscometer linked to each other by U type facilitate the free full of liquid at atmospheric pressure. Viscosity values (η) of pure liquids and their binary mixtures are calculated using the solution. The accuracy in viscosity data was ± 0.0005 mPa.s. The flow time of pure liquids and liquid mixtures were repeated for five times. The efflux Time was measured with an electronic stopwatch (Racer) with a time resolution (± 0.015), and an average of at least five flow time readings was taken.

The measured values of viscosities of pure 1,3-dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol compare well with the corresponding literature values.

3. Theoretical

The experimentally measured ultrasonic velocity (u), density (ρ) and viscosity (η) are used to evaluate derived parameters like molar volume (V_m), adiabatic compressibility (β_{ad}), and acoustic impedance (Z) using well established relations.

The deviation in viscosities (Δη) can be computed using the relationship.

$$\Delta\eta = \eta - \sum_{i=1}^{i}(X_i\eta_i) \quad (1)$$

where η is the dynamic viscosities of the mixture and x_i, η_i are the mole fraction and viscosity of i^{th} component in the mixture, respectively. The estimated uncertainty for viscosity deviation (Δη) is ±0.004mPa.s.

The molar volume (V_m) of binary liquid mixtures were calculated by using a following equation:

$$V_m = \frac{(X_1M_1 + X_2M_2)}{\rho} \quad (2)$$

The adiabatic compressibility (β_{ad}) has been calculated from the ultrasonic velocity (u) and density (ρ) of the medium using the equation as

$$\beta_{ad} = \frac{1}{u^2\rho} \quad (3)$$

The excess adiabatic compressibility (β_{ad}^E) values were obtained by subtracting the ideal values from the experimental values.

$$\beta_{ad}^E = \beta_{ad\ exp.} - X_1\,\beta_{ad\,(1)} + X_2\,\beta_{ad\,(2)}$$

where β_{ad} is the adiabatic compressibility of the mixture and X_1, X_2, $\beta_{ad\,(1)}$, $\beta_{ad\,(2)}$ are the mole fraction and adiabatic compressibility of component 1 and 2 in the mixture, respectively.

The acoustic impedance is the parameter related to elastic properties of the medium and calculated by using the expression.

$$Z = \rho.\ U \quad (4)$$

where ρ is the density and u is the sound velocity.

The excess acoustic impedance (Z^E) values were obtained by subtracting the ideal values from the experimental values.

$$Z^E = Z_{exp..} - X_1\,Z_{(1)} + X_2\,Z_{(2)}$$

where Z is the acoustic impedance of the mixture and X_1, X_2, Z_1, Z_2 are the mole fraction and acoustic impedance of component 1 and 2 in the mixture, respectively.

The excess value of ultrasonic related parameters has been calculated by using the following relation

$$A^E = A_{exp.} - (X_1A_1 + X_2A_2) \quad (5)$$

Where A represents the parameter such as intermolecular free length, molar volume, isentropic compressibility, viscosity and internal pressure and X_1 and X_2 is the mole fractions of components whose parameters.

4. Result and Discussion

The experimentally determined values of density (ρ), sound velocity (u) and viscosity (η) and derived parameters adiabatic compressibility(β_{ad}), molar volume (V_m) and acoustic impedance (Z) at 298.15K and atmospheric pressure for the binary liquid system 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are listed in table 3. The same excess values for the binary liquid mixtures 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are presented in table 4. The data related to excess adiabatic compressibility, excess viscosity and excess acoustic impedance for the binary liquid system 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol were graphically represented in figures 1 to 3 at 298.15K respectively. Alcohols are good solvent that can dissolve both the polar and non-polar components. The

hydrophilic –OH group of alcohols can dissolve the polar whereas the short hydrophobic hydrocarbon group can dissolve the non-polar.

Alcohols are strongly self-associated liquids with a three dimensional network of hydrogen bonds and can be associated with any other group having some degree of polar attraction. The associative alcohols molecule act as proton donar enabling hydrogen bonding with 1,3- dioxolane molecule. In the system studied, the complex formation is likely to occur between $H^{\delta+}$ of alcohol and $O^{\delta-}$ of ether group of 1,4-dioxane. Hence in the present study there is existence of solute-solvent interactions.

From the table 3, it was observed that the density and ultrasonic velocity increase with increasing mole fraction of 1,3-Dioxolane while the viscosity decrease. This may be due to association of a very strong dipole- induced dipole interaction between the component molecules.

Table 3. *Experimental Values of density (ρ), sound velocity (u) and viscosity (η), derived parameters adiabatic compressibility (β_{ad}), molar volume (V_m) and acoustic impedance (Z) for the binary mixtures of 1,3-Dioxolane(1) + Alkanols (2) at 298.15K and atmospheric pressure.*

Mole fraction 1,3-Dioxolane (x_1)	Density (ρ) $g.cm^{-3}$	Sound velocity (u) ms^{-1}	Viscosity (η) mPa.s	adiabatic compressibility(β_{ad}) × $10^{-7}Pa^{-1}$	molar volume (V_m) × 10^{-3} $cm^3.mole^{-1}$	acoustic impedance (Z) × 10^{-4} $g.cm.s^{-1}$
1,3-Dioxolane + Pentanol						
0	0.8124	1198	3.3978	8.5770	0.1085	0.0973
0.0939	0.8276	1284	2.3973	7.3290	0.1049	0.1062
0.1942	0.8436	1290	1.8970	7.1233	0.1012	0.1088
0.2941	0.8640	1296	1.4437	6.8909	0.0972	0.1119
0.3942	0.8836	1300	1.1866	6.6966	0.0934	0.1148
0.4787	0.9068	1304	1.0904	6.4853	0.0897	0.1182
0.5999	0.9316	1310	0.9311	6.2551	0.0855	0.1220
0.6972	0.9596	1318	0.7717	5.9991	0.0816	0.1264
0.7928	0.9876	1324	0.7171	5.7762	0.0779	0.1307
0.9035	1.0260	1332	0.6489	5.4934	0.0735	0.1366
1.0000	1.0616	1340	0.5885	5.246	0.0697	0.1422
1,3-Dioxolane + Hexanol						
0	0.8176	1306	4.6091	7.1709	0.1249	0.1067
0.0912	0.8252	1317	3.3826	6.9867	0.1207	0.1086
0.1955	0.8432	1320	2.3306	6.8065	0.1146	0.1113
0.2923	0.8584	1322	1.9839	6.6657	0.1094	0.1134
0.3982	0.8792	1325	1.5720	6.4786	0.1034	0.1164
0.4942	0.8992	1327	1.3059	6.3154	0.0981	0.1193
0.6059	0.9264	1330	1.0343	6.1024	0.0919	0.1232
0.6976	0.9508	1332	0.9131	5.9279	0.0868	0.1266
0.8018	0.9836	1335	0.7680	5.7045	0.0809	0.1313
0.8914	1.0168	1337	0.7304	5.5018	0.0758	0.1359
1.0000	1.0616	1340	0.5885	5.2460	0.0697	0.1422
1,3-Dioxolane + Heptanol						
0	0.8196	1325	5.9066	6.9497	0.1417	0.1085
0.0928	0.8304	1334	4.3181	6.7671	0.1352	0.1107

Mole fraction 1,3-Dioxolane (x_1)	Density (ρ) $g.cm^{-3}$	Sound velocity (u) ms^{-1}	Viscosity (η) mPa.s	adiabatic compressibility(β_{ad}) × $10^{-7}Pa^{-1}$	molar volume (V_m) × 10^{-3} $cm^3.mole^{-1}$	acoustic impedance (Z) × 10^{-4} $g.cm.s^{-1}$
0.1905	0.8412	1334	3.2577	6.6802	0.1286	0.1122
0.2939	0.8592	1335	2.5895	6.5304	0.1208	0.1147
0.3894	0.8740	1335	1.9926	6.4199	0.1141	0.1166
0.4818	0.8916	1336	1.5315	6.2837	0.1075	0.1191
0.6021	0.9184	1337	1.2190	6.0912	0.0989	0.1227
0.6952	0.9420	1337	1.0959	5.9387	0.0922	0.1259
0.7892	0.9756	1338	0.9903	5.7255	0.0850	0.1305
0.9006	1.0156	1339	0.7057	5.4918	0.0770	0.1359
1.0000	1.0616	1340	0.5885	5.2460	0.0697	0.1422
1,3-Dioxolane + Octanol						
0	0.8296	1350	7.1508	6.6622	0.1581	0.1111
0.0885	0.8296	1350	5.6095	6.6139	0.1509	0.1119
0.1967	0.8464	1349	3.9321	6.4923	0.1408	0.1141
0.2998	0.8560	1348	3.2616	6.4291	0.1324	0.1153
0.3902	0.8712	1348	2.4284	6.3168	0.1243	0.1174
0.4963	0.8876	1348	1.9058	6.2002	0.1153	0.1196
0.6008	0.9140	1347	1.3631	6.0301	0.1055	0.1231
0.6925	0.9340	1348	1.1376	5.8921	0.0978	0.1259
0.7975	0.9676	1348	0.9141	5.6875	0.0883	0.1304
0.8940	1.0104	1348	0.7652	5.4466	0.0792	0.1362
1.0000	1.0616	1340	0.5885	5.2460	0.0697	0.1422
1,3-Dioxolane + Nonanol						
0	0.8248	1366	8.9258	6.4976	0.1749	0.1126
0.0876	0.8336	1366	6.8601	6.4289	0.1656	0.1138
0.1913	0.8404	1363	5.8531	6.4051	0.1556	0.1145
0.2942	0.8504	1359	4.4022	6.3671	0.1453	0.1155
0.3963	0.8692	1355	3.1558	6.2662	0.1339	0.1177
0.4959	0.8844	1352	2.3340	6.1859	0.1237	0.1195
0.6050	0.9092	1349	1.7321	6.0439	0.1119	0.1226
0.6947	0.9332	1346	1.3334	5.9145	0.1023	0.1256
0.7993	0.9648	1343	0.9642	5.7466	0.0913	0.1295
0.9013	1.0084	1340	0.8031	5.5228	0.0803	0.1351
1	1.0616	1340	0.5885	5.2460	0.0697	0.1422
1,3-Dioxolane + Decanol						
0	0.8292	1378	11.8027	6.4976	0.1908	0.1142
0.0881	0.8364	1374	8.5615	6.4289	0.1803	0.1149
0.191	0.8396	1370	7.8207	6.4051	0.1693	0.1150

Mole fraction 1,3-Dioxolane (x_1)	Density (ρ) $g.cm^{-3}$	Sound velocity (u) ms^{-1}	Viscosity (η) mPa.s	adiabatic compress-ibility(β_{ad}) × $10^{-7}Pa^{-1}$	molar volume (V_m) × 10^{-3} $cm^3.mole^{-1}$	acoustic im-pedance (Z) × 10^{-4} $g.cm.s^{-1}$
0.2921	0.8560	1366	5.5340	6.3671	0.1561	0.1169
0.3937	0.8672	1362	4.2319	6.2662	0.1442	0.1181
0.4956	0.8824	1358	3.4173	6.1859	0.1320	0.1198
0.604	0.9076	1353	2.5370	6.0439	0.1183	0.1227
0.7129	0.9308	1348	1.5262	5.9145	0.1055	0.1254
0.7983	0.9616	1344	1.1637	5.7466	0.0946	0.1292
0.8971	1.0040	1340	0.8623	5.5228	0.0824	0.1345
1	1.0616	1340	0.5885	5.246	0.0697	0.1422

Table 4. *Excess adiabatic compressibility (β_{ad}^E), excess viscosity (η^E), excess molar volume (V_m^E) and excess acoustic impedance (Z^E) for the binary mixtures of 1,3-Dioxolane (1) + Alkanols (2) at 298.15K and atmospheric pressure.*

Mole fraction 1,3-Dioxolane (x_1)	Excess adiabatic com-pressibility (β_{ad}^E) × $10^{-7}Pa^{-1}$	excess viscosity (η^E) mPa.s	Excess molar volume (V_m^E) × 10^{-3} $cm^3.mole^{-1}$	Excess acoustic impedance (Z^E) × 10^{-4} $g.cm.s^{-1}$
1,3-Dioxolane + Pentanol				
0	-	-	-	-
0.0939	-93.514	-0.7367	0.0469	47.19498
0.1942	-80.677	-0.9552	0.2682	27.73692
0.2941	-70.644	-1.1280	0.1192	14.35296
0.3942	-56.727	-1.1038	0.2446	-1.68484
0.4787	-49.711	-0.9627	0.1860	-5.86255
0.5999	-32.372	-0.7815	0.2867	-22.3876
0.6972	-25.563	-0.6675	0.1314	-21.7466
0.7928	-15.997	-0.4535	0.1568	-21.869
0.9035	-7.400	-0.2108	0.0076	-12.5556
1.0000	-	-	-	-
1,3-Dioxolane + Hexanol				
0	-	-	-	-
0.0912	-12.864	-0.8597	0.7779	-13.3654
0.1955	-11.193	-1.4925	0.4810	-24.1169
0.2923	-93.762	-1.4500	0.6245	-36.6767
0.3982	-77.201	-1.4361	0.4952	-44.1104
0.4942	-61.541	-1.3162	0.4919	-49.8688
0.6059	-45.638	-1.1387	0.3860	-50.6217
0.6976	-32.537	-0.8912	0.3783	-48.7995
0.8018	-20.169	-0.6174	0.2564	-39.1249
0.8914	-1.060	-0.2947	0.0816	-24.5556

Mole fraction 1,3-Dioxolane (x_1)	Excess adiabatic compressibility (β_{ad}^{E}) $\times 10^{-7}$ Pa^{-1}	excess viscosity (η^{E}) mPa.s	Excess molar volume (V_m^{E}) $\times 10^{-3}$ cm^3.mole^{-1}	Excess acoustic impedance (Z^{E}) $\times 10^{-4}$ g.cm.s^{-1}
1.0000	-	-	-	-
1,3-Dioxolane + Heptanol				
0	-	-	-	-
0.0928	2.457	-1.0951	0.1293	-9.44037
0.1905	5.504	-1.6358	0.5357	-27.9265
0.2939	8.146	-1.7541	0.2168	-37.8571
0.3894	13.359	-1.8431	0.4437	-50.2419
0.4818	15.486	-1.8128	0.4770	-56.9538
0.6021	16.733	-1.4856	0.4818	-60.7204
0.6952	17.334	-1.1136	0.5437	-60.5022
0.7892	12.039	-0.7193	0.0752	-46.2414
0.9006	7.647	-0.4114	0.1264	-29.2001
1.0000	-	-	-	-
1,3-Dioxolane + Octanol				
0	-	-	-	-
0.0885	7.713	-1.0951	0.6846	-19.3955
0.1967	10.869	-1.6358	0.0682	-31.1779
0.2998	19.142	-1.7541	0.8340	-51.1151
0.3902	20.728	-1.8431	0.6824	-58.7113
0.4963	24.082	-1.8128	1.0462	-69.5677
0.6008	21.867	-1.4856	0.5270	-67.3609
0.6925	21.066	-1.1136	0.8545	-67.9767
0.7975	15.476	-0.7193	0.6410	-55.3057
0.8940	5.051	-0.4114	0.0624	-27.5923
1.0000	-	-	-	-
1,3-Dioxolane + Nonanol				
0	-	-	-	
0.0876	4.101	-1.3354	-0.0127	-13.8972
0.1913	14.688	-1.4778	0.8880	-37.811
0.2942	23.767	-2.0708	1.3824	-58.0273
0.3963	26.458	-2.4659	0.7277	-66.163
0.4959	30.889	-2.4573	0.9917	-77.6885
0.6050	30.351	-2.1496	0.6632	-79.1657
0.6947	28.662	-1.8005	0.4673	-76.1285
0.7993	24.941	-1.2976	0.5023	-67.4371
0.9013	15.325	-0.6083	0.1749	-42.0859
1	-	-	-	
1,3-Dioxolane + Decanol				

Mole fraction 1,3-Dioxolane (x_1)	Excess adiabatic compressibility (β_{ad}^{E}) $\times 10^{-7}$ Pa^{-1}	excess viscosity (η^{E}) mPa.s	Excess molar volume (V_m^E) $\times 10^{-3}$ cm^3.mole^{-1}	Excess acoustic impedance (Z^{E}) $\times 10^{-4}$ g.cm.s^{-1}
0	-	-	-	
0.0881	7.94	-2.2532	0.2115	-18.0838
0.191	20.585	-1.8401	1.6598	-45.848
0.2921	23.249	-2.9930	0.7076	-55.1023
0.3937	30.026	-3.1558	1.1236	-71.7103
0.4956	34.182	-2.8276	1.2487	-83.06
0.604	33.522	-2.4923	0.6457	-83.7183
0.7129	34.915	-2.2819	1.0260	-87.4645
0.7983	28.826	-1.6867	0.5040	-73.6965
0.8971	18.727	-0.8801	0.1778	-48.3816
1	-	-	-	-

Excess Molar Volume (V_m^E)

The excess molar volume (V_m^E) data of all the binary mixtures of 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are presented in table 4 at 298.15K and atmospheric pressure.

Excess molar volumes can be used for understanding some of the molecular interactions (such as dispersion forces, hydrogen bonding interactions) in the binary mixtures. The excess molar volume data is a helpful parameter in the design of technological processes of a reaction, and can be used to predict vapour liquid equilibria using appropriate equation of state models. The measurement of molar volume in binary liquid mixture provides same reliable information in the study of molecular interaction.

A perusal of table 4 indicates that the values of excess molar volume (V_m^E) data for the binary mixtures of 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are positive.

The excess molar volume (V_m^E) of the binary mixtures investigated in the study were all positive over the entire range of solvent composition at 298.15 K. These are shown in Table 4. The positive excess molar volume (V_m^E) are attributable mainly to the association between the1,3-Dioxolane and alkanol through inter molecular hydrogen bonding between the –OH groups in alkanol and the oxygen atoms in the1,3-Dioxolane molecule. The magnitudes of the positive excess molar volumes were in the order Pentanol < Hexanol < Heptanol < Octanol < Nonanol < Decanol for the binary mixtures with the1,3-Dioxolane. The strength of the associations arising from the interactions between the unlike molecules was stronger than the strength of the association between like molecule. Large positive excess molar volume (V_m^E) for binary mixture of1,3-Dioxolane with alcohols have also been reported by other workers. It has been suggested that the large positive values are due to hetero association of unlike molecules which give rise to formation of cross complexes where O-H---O bonds of the mixtures are stronger than O---H-O bonds of the single component solvents. It is generally increases with chain length. This suggest that the oxygen atom in the alkanols in electron enriched to different degrees depending upon the chain length and degree of the alkyl group attached to the oxygen atom in the alkanols.

The positive values of excess molar volume (V_m^E) indicate that there is a volume expansion. This signifies that the mixtures are less compressible than the corresponding ideal mixtures. Further, it is observed the magnitude of positive excess molar volume (V_m^E) values decrease with increase in composition of 1,3-Dioxolane. According to Marcus [25], the molecules of alkanols are associated through hydrogen bonding in pure state. Mixing these alcohol molecules with polar molecule like 1,3-Dioxolane would induce mutual dissociation of the hydrogen-bonded structure present in pure alcohols with subsequent formation of inter molecular hydrogen bonds (O-----OH) between the oxygen atom of ether group of 1,3-Dioxolane molecule and hydrogen atom of hydroxyl group of alcohols. The positive excess molar volume (V_m^E) values suggest that the higher alcohols less proton donating ability than the lower alcohols. Hence hetro association affects decrees in the binary liquid mixtures with an increase of chain length of linear alcohols. The algebraic values of excess molar volume (V_m^E) for the mixtures of 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol fall in the order,

Pentanol < Hexanol < Heptanol < Octanol < Nonanol < Decanol

Excess adiabatic compressibility (β_{ad}^{E})

The values of excess adiabatic compressibility (β_{ad}^{E}), may be

interpreted in terms of two opposing effects viz. (i) loss of mutual dipolar association and difference in size and shape of unlike components molecules, and (ii) dipole-induced dipole and dipole- dipole interactions. The former effect contributes to an increase in free lengths of component mixtures described by Jacobson. This leads to negative deviation in sound velocity and positive deviation in isentropic compressibility. The latter effect, on the other hand contributes to positive deviation in sound speed and negative deviation in isentropic compressibility. The sign and magnitude of the actual deviation depend on the relative strength or the two opposing effects.

The excess adiabatic compressibility (β_{ad}^{E}) data of all the binary mixtures of 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are graphically presented Figure 1 at 298.15 K and atmospheric pressure. An examination of curves in Figure 1 shows that the values of excess adiabatic compressibility (β_{ad}^{E}) data for 1,3-Dioxolane with Pentanol, Hexanol, are negative and for the remaining binary mixtures excess adiabatic compressibility (β_{ad}^{E}) is positive over the entire composition range at 298.15 K. It is evident that the excess adiabatic compressibility (β_{ad}^{E}) values are negative for lower monoalcohols, but the magnitude of the negative values diminishes and the positive values increase with increasing chain length of the alcohols. The order it is follows is:

Pentanol < Hexanol < Heptanol < Octanol < Nonanol < Decanol

The excess adiabatic compressibility (β_{ad}^{E}) values were ascribed according to Sri Devi et al [26] the negative excess values have been due to the closely packed molecules which account for existence of strong molecular interaction where as positive excess values are due to prevailing of dispersion forces [27] between unlike molecules.

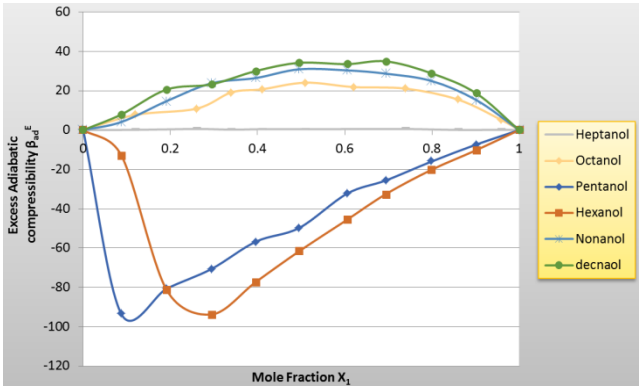

Figure 1. *Curves of adiabatic compressibility (β_{ad}^{E}) against the mole fraction of 1,3-dioxolane x_1, for the binary mixture (1,4-dioxane (1) + Alkanols (2)) at 298.15K and atmospheric pressure. The solid lines represent the values calculated from the Redlich−Kister equation.*

A perusal of curves in Figure 1 shows that the excess adiabatic compressibility (β_{ad}^{E}) negative value decreases may be attributed to hetero association complexes decrease with increasing chain length, probably due to less proton-donating ability of higher alcohols. Experimental results suggest that the negative values of excess adiabatic compressibility (β_{ad}^{E}) and deviation in intermolecular free length (ΔL_f) for binary mixtures attributed to the dipole-dipole interactions through formation of complexes between the molecules of mixing components and the positive values of excess adiabatic compressibility (β_{ad}^{E}) and deviation in intermolecular free length (ΔL_f) for binary mixtures may be due to the domination ofdispersion forces over formation of complexes between unlike molecules.

The excess adiabatic compressibility (β_{ad}^{E}) values of 1,3-Dioxolane with alcohols fall in the order:

Decanol < Nonanol < Octanol < Heptanol < Hexanol < Pentanol

Excess Viscosity (η^{E})

The excess viscosity (η^{E}) data of all the binary mixtures of 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are graphically presented Figure 2 at 298.15 K and atmospheric pressure. An examination of curves in Figure 2 shows that the values of excess viscosity (η^{E}) data for 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are negative over the entire composition range at 298.15 K.

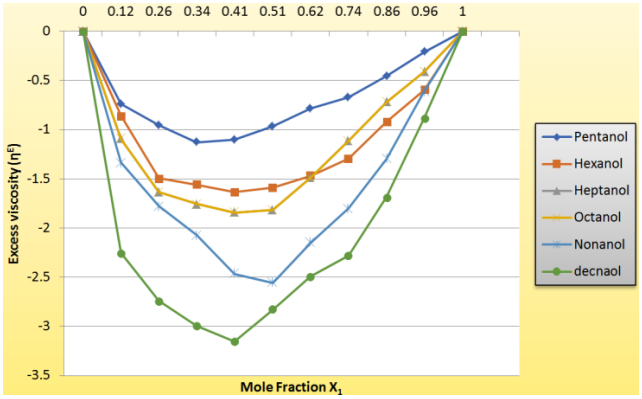

Figure 2. *Curves of excess viscosity (η^{E}) against the mole fraction of 1,3-dioxolane x_1, for the binary mixture (1,4-dioxane (1) + Alkanols (2)) at 298.15K and atmospheric pressure. The solid lines represent the values calculated from the Redlich−Kister equation.*

The measurement of viscosity in binary liquid mixture provides some reliable information in the study of molecular interaction. Table 3 shows that the viscosity decrease with increase in concentration of 1,3-Dioxolane molecule. More insight about molecular interaction can be obtained by excess viscosity (η^{E}) values.

According to Fort and Moore, the excess viscosity gives the strength of the molecular interaction between the interacting molecules. The excess value of viscosity at the six

binary mixtures 1,3-Dioxolane + Pentanol, 1,3-Dioxolane + Hexanol, 1,3-Dioxolane + Heptanol, 1,3-Dioxolane + Octanol, 1,3-Dioxolane + Nonanol and 1,3-Dioxolane + Decanol at the 298.15 K are reported in Table 4. The Figure 2 represents the variation of excess viscosity (η^E) is found to be negative for all six binary liquid mixtures over the entire composition range at the 298.15 K. Which suggest the presence of weak intermolecular interactions. For systems where dispersion, induction and dipolar forces are operating, the values of excess viscosity are found to be negative, whereas the existence of specific interaction leading to the formation of complexes in mixtures tends to make positive. The excess viscosity is negative through the whole range of concentration in all the studied systems. The large negative values of excess viscosity for all systems can be attributed to the presence of dispersion, induction and dipolar forces between the components.

The negative excess viscosity (η^E) for all the six binary liquid mixtures (1,3-Dioxolane + Pentanol, 1,3-Dioxolane + Hexanol, 1,3-Dioxolane + Heptanol, 1,3-Dioxolane + Octanol, 1,3-Dioxolane + Nonanol and 1,3-Dioxolane + Decanol) studied are indicative of the predominance of dispersion forces and further their magnitudes increase from pentanol to decanol (C_5-C_{10}), hence suggesting an increase in dispersion forces in the same order. Alcohols are good solvent that can dissolve both the polar and non-polar components. The hydrophilic –OH group of alcohols can dissolve the polar whereas the short hydrophobic hydrocarbon group can dissolve the non-polar. Alcohols are strongly self-associated liquids with a three dimensional network of hydrogen bonds and can be associated with any other group having some degree of polar attraction. The associative alcohols molecule act as proton donor enabling hydrogen bonding with 1,3-Dioxolane molecule. In the system studied, the complex formation is likely to occur between $H^{\delta+}$ of alcohol and $O^{\delta-}$ of ether group of 1,3-Dioxolane. Hence in the present study there is existence of solute-solvent interactions. The algebraic values of excess viscosity for binary mixtures of 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol fall in the order:

Decanol < Nonanol < Octanol < Heptanol < Hexanol < Pentanol

In the alkanol mixture, the 1,3-Dioxolane is completely dissolved and so no changes of hydrogen bond raptures and only the interaction with the 1,3-Dioxolane ring and the active group of alkanols, which are mostly dispersive in nature. The increase in mole fraction of 1,3-Dioxolane increase the net dispersive interaction and hence the velocity continuously increases as observed. As the mole fraction of 1,3-Dioxolane increases, the hydrogen bond repture of the boat form is of considerable extent and they leads to additional dipole type interaction. 1,3-Dioxolane being non-polar the predominant dispersive type interactions with temporary dipolar type are existing as a net result of intermolecular forces in all systems.

Acoustic impedance (Z)

The excess acoustic impedance (Z^E) data of all the binary mixtures of 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are graphically presented Figure 3 at 298.15 K and atmospheric pressure. An examination of curves in Figure 3 shows that the values of excess acoustic impedance (Z^E) data for 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are negative over the entire composition range at 298.15 K.

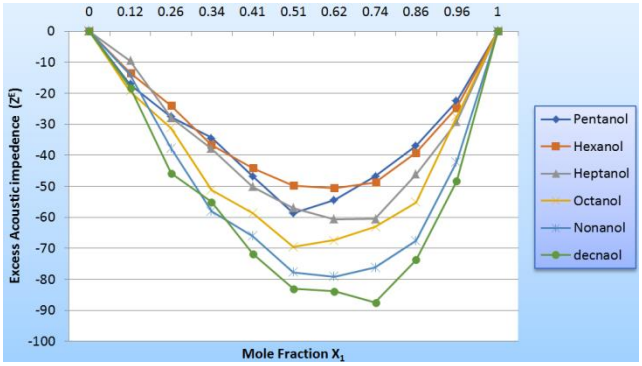

Figure 3. *Curves of excess acoustic impedance (Z^E) against the mole fraction of 1,3-dioxolane x_1, for the binary mixture (1,4-dioxane (1) + Alkanols (2)) at 298.15K and atmospheric pressure. The solid lines represent the values calculated from the Redlich−Kister equation.*

The variation of excess acoustic impedance (Z^E) with mole fraction of 1,3-Dioxolane at 298.15K are shown in figure 3. It is observed the excess acoustic impedance (Z^E) data for 1,3-Dioxolane with Pentanol, Hexanol, Heptanol, Octanol, Nonanol and Decanol are negative over the entire composition range at 298.15 K. This is in agreement with requirement as both ultrasonic velocity and density increase with increase in concentration of the solute and also effective due to solute – solvent interaction.

5. Conclusions

From experimental results, negative excess molar volume (V_m^E) and excess adiabatic compressibility (β_{ad}^E) values can be attributed to the dipole –dipole interactionsbetween unlike molecules through hydrogen bonding and positive values indicate that the effect due to breaking up of self-associated structures of the components of the mixtures is dominant over the effect of H-bonding and dipole-dipole interaction between unlike molecules The positive values of Excess molar volume (V_m^E) and excess adiabatic compressibility (β_{ad}^E) may be attributed to the formation of hydrogen bonding (O-H….O) resulting in the formation of complexes between the component molecules and negatives values suggesting breaking of the self-associated alcohols and weak interactions between unlike molecules. From these data, several thermodynamic excess functions have been calculated and correlated using the

Redlich – Kister type polynomial equation. The sign and magnitude of these quantities have been discussed in terms of hydrogen bond, electron-transfer complexes and di-pole-dipole interactions between the component molecules.

Abbreviations

ρ	Density of Liquid
u	Sound Velocity
u^E	Excess Sound Velocity
η	Viscosity
η^E	Excess Viscosity
β_{ad}	Adiabatic Compressibility
β_{ad}^E	Excess Adiabatic Compressibility
V_m	Molar Volume
V_m^E	Excess Molar Volume
Z	Acoustic Impedance
Z^E	Excess Acoustic Impedance
X_1	Mole Fraction of 1,3-Dioxolane
Y^E	Thermodynamic Excess Function

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Author Contributions

Ravi Kant Mishra: Data curation, Investigation

Dhirendra Kumar Sharma: Methodology, Supervision, Writing – original draft

Chandra Pal Prajapati: Formal Analysis, Software

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Data Availability Statement

All data generated or analyzed during this study are included in this published article.

Conflicts of Interest

The authors declare no conflicts of interest.

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